

Luminescent Ni(0) complexes

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Abstract

With its $3d^{10}$ valence electron configuration Ni(0) is isoelectronic with Cu(I). While many Cu(I) complexes emitting from metal-to-ligand charge transfer (MLCT) excited states have been explored, the number of luminescent Ni(0) complexes known to date is very limited. Ni(0) is typically stabilized by carbonyls, phosphines or isocyanides due to the π -acceptor properties of these ligands, and photoluminescence has been reported in a few selected cases that are reviewed herein. Recent studies indicate that chelating isocyanide ligands are promising for obtaining Ni(0) complexes with long-lived $^3\text{MLCT}$ states, and this could be interesting for a similar range of applications as with photoactive Cu(I) complexes, including for example luminescent devices, solar cells, and organic photoredox reactions.

Keywords

metal-to-ligand charge transfer; isocyanide, phosphine; *N*-heterocyclic carbene; π -acceptor; earth-abundant metal element

Abbreviations

dbiy, 1,3-di-*t*-butylimidazol-2-ylidene; dpp, 2,9-diphenyl-1,10-phenanthroline; dppe, 1,2-bis(diphenylphosphino)ethane; MLCT, metal-to-ligand charge transfer; NHC, *N*-heterocyclic carbene; PPh₃, triphenylphosphine; P(OPh)₃, triphenylphosphite; P(*O*-*o*-cresyl)₃, tri(*o*-xylyl)phosphite.

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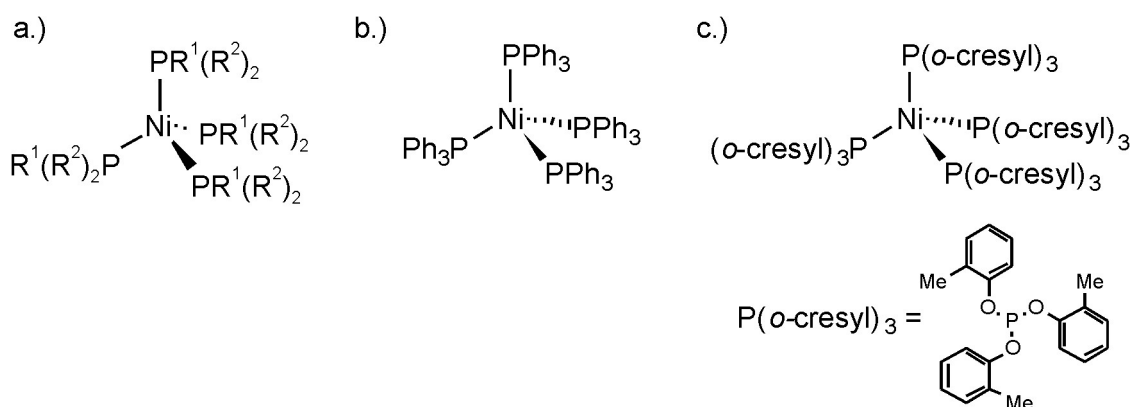
1. Introduction

The photophysics and the photochemistry of Cu(I) complexes with long-lived $^3\text{MLCT}$ excited states have received significant attention over the past few decades [1-4]. Cu(I) is an attractive earth-abundant alternative to traditional d^6

³MLCT emitters made from precious metals such as Ru(II), Re(I), Os(II), and Ir(III) [5]. While many initial studies of emissive Cu(I) complexes focused on basic photophysical aspects such as the distortion in the MLCT excited states [6-9], more recent studies tend to put a stronger emphasis on possible applications. This includes for example the use of Cu(I) complexes as luminophores in light emitting devices [10, 11], as dyes in solar cells [12], and as sensitizers for organic photoredox conversions [4, 13, 14]. At the same time, isoelectronic Ni(0) complexes have received very little attention, despite the fact that similarly favorable excited-state properties could be anticipated. Herein we provide a survey over the currently known luminescent Ni(0) complexes and discuss their properties in the context of other MLCT emitters made from earth-abundant metals.

2. From early structural studies to emissive complexes

The low oxidation state of Ni(0) asks for stabilization by π -acceptor ligands such as carbonyl, isocyanides, phosphines, or phosphites. Ni(CO)₄ can be considered the prototype of a tetrahedral Ni(0) complex and some analogous isocyanide complexes have long been known [15-17]. Early infrared spectroscopic studies demonstrated that isocyanides can indeed simultaneously act as good σ -donors and π -acceptors to Ni(0). These initial IR studies also indicated that the actual point symmetry of the Ni(CNC)₄ groupings in homoleptic complexes with monodentate isocyanide ligands is lower than T_d, compatible with the view that the M-C-N-C entities are nonlinear as a result of the metal-carbon π -bonding [18]. Initial studies focused on tetrakis(arylisocyanide) complexes of Ni(0), whereas tetrakis(alkylisocyanide) complexes became accessible in analytically pure form somewhat later [19, 20]. Crystallographic studies of different tetrakis(arylisocyanide)nickel(0) complexes provided direct evidence for the anticipated slightly distorted structures [21, 22], and in one rather special case a macrocyclic tetra-arylisocyanide complex of Ni(0) was reported [23]. More recent studies of Ni(0) isocyanide complexes have focused on coordinatively unsaturated Ni(CNR)₃ complexes as isolable analogues of unsaturated metal carbonyls, such as for example Ni(CO)₃ or Fe(CO)₄ [24-27]. However, the potential luminescence properties of Ni(0) isocyanide complexes did not seem to receive any attention until very recently [28].



Scheme 1. Molecular structures of some Ni(0) complexes investigated in the context of luminescence in the early literature [29, 30].

By contrast, luminescent Ni(0) phosphine complexes were already reported by Dori nearly 50 years ago [29]. The respective early study explored more than 50 different d¹⁰ metal complexes with phosphine and arsine ligands. In

addition to Ni(0), complexes with several other d^{10} metals were investigated, including Pd(0), Pt(0), Cu(I), Ag(I), Au(I), Zn(II), Cd(II), and Hg(II). The study reported that, in the solid state at 77 K, all of these complexes exhibited luminescence after irradiation with a mercury-vapor lamp, although quenching was observed for Ag(I), Au(I), Cd(II), and Hg(II) at higher temperatures [29]. The general structure of the Ni(0) complexes was as represented in Scheme 1a with R^1 = phenyl or substituted phenyl and R^2 = aryl, alkyl, cycloalkyl and alkoxy. Unfortunately, actual luminescence spectra of Ni(0) complexes were not shown in this short communication. However, it was noted that the emission is likely due to $d \rightarrow \pi^*$ charge-transfer type excitations [29].

The first report of Ni(0) phosphine and phosphite complexes which possess long-lived emissive excited states in fluid solution at room temperature appeared in 1985 [30]. THF solutions of $Ni(PPh_3)_4$ and $Ni(P(O-o-cresyl)_3)_4$ (Scheme 1b, c) were reported by Caspar to show luminescence with band maxima at 740 and 645 nm, respectively. For the latter, an excited-state lifetime of 5.13 μs and a luminescence quantum yield of 0.293% in N_2 -saturated THF solution at 25 $^{\circ}C$ was reported [30]. However, several lines of evidence indicated that in the investigated class of NiL_4 , PdL_4 , and PtL_4 complexes the luminescence originates from species that are three-coordinate in both the ground and excited states. This interpretation made sense, since it was known that in solution the respective ML_4 complexes exist in equilibrium with ML_3 and ML_2 species. Luminescence quantum efficiencies were found to decrease upon addition of excess ligand, compatible with the view that coordinatively unsaturated species are the emitters. Organic triplet acceptors did quench the luminescence with rates depending systematically on the triplet energies of the organic acceptors, indicating that the emission originates from triplet states. The relative insensitivity of the observed emission spectra to the nature of the phosphine, phosphite, and arsine ligand for a given metal (either Ni(0), Pd(0), or Pt(0)) suggested that the excited state is largely metal-localized in character. Based on extended Hückel calculations it was hypothesized that the lowest excited state for planar ML_3 d^{10} complexes involves the promotion of an (n) d-electron to a vacant metal-localized (n+1) p-orbital [30]. In light of studies on Cu(I) complexes it seems possible that THF solvent molecules can weakly coordinate to these ML_3 complexes [9].

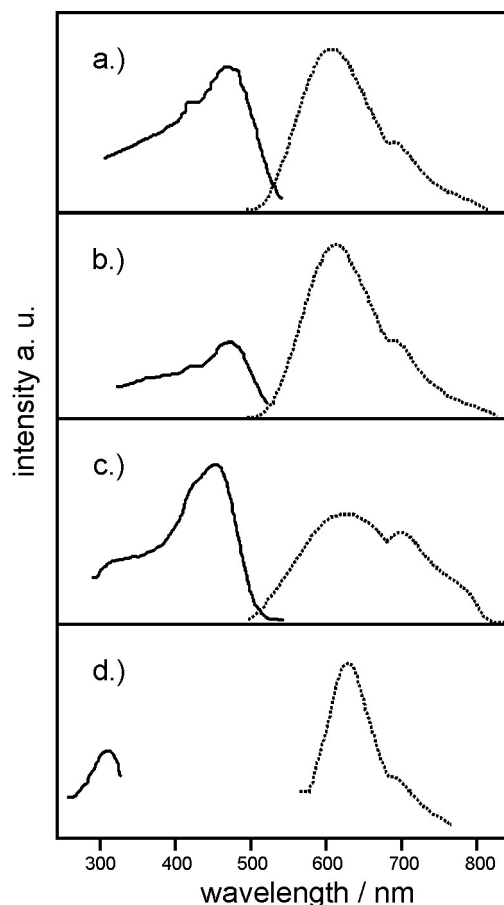


Figure 1. Excitation (solid lines) and luminescence (dotted lines) spectra of (a) $\text{Ni}(\text{dppe})_2$; (b) $\text{Ni}(\text{CO})_2(\text{AsPh}_3)_2$; (c) $\text{Ni}(\text{CO})_2(\text{SbPh}_3)_2$; (d) $\text{Ni}(\text{CO})_2(\text{P}(\text{OPh})_3)_2$ at room temperature in the solid state [31].

The next report on luminescent $\text{Ni}(0)$ complexes appeared 12 years later in a comparative study of $\text{Ni}(\text{dppe})_2$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$), $\text{Ni}(\text{CO})_2(\text{SbPh}_3)_2$, and NiL_4 with $\text{L} = \text{AsPh}_3$, SbPh_3 , $\text{P}(\text{OPh})_3$ by Frem and coworkers [31]. These complexes were synthesized from a $\text{Ni}(\text{II})$ source using NaBH_4 as a reducing agent. $\text{Ni}(\text{AsPh}_3)_4$ could be stored in stoppered vials for 3 years, $\text{Ni}((\text{OPh})_3)_4$ was found to decompose over the period of a few days, and $\text{Ni}(\text{SbPh}_3)_4$ decomposed instantly when exposed to air. All complexes exhibited orange luminescence in the solid state and in fluid solution at room temperature. From the solid-state excitation and emission spectra in Figure 1 it is seen that there are fairly large Stokes shifts of ca. $11'000\text{ cm}^{-1}$, and this was interpreted in terms of luminescence from a spin-forbidden transition. Given the π -accepting characters of the ligands, the emissive excited state was assigned to $^3\text{MLCT}$. Luminescence lifetimes could not be determined due to instrumental limitations.

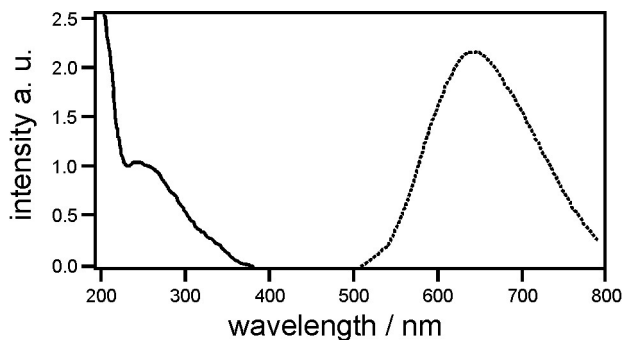
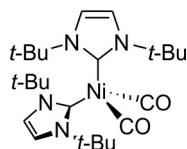


Figure 2. Absorption (solid line) and luminescence (dotted line) spectra of $\text{Ni}(\text{PPh}_3)_2(\text{CO})_2$. Absorption was recorded in CH_3CN at room temperature, emission in the solid state at 77 K [32].

The structurally related $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ complex was investigated in the year 2000 by Kunkely and Vogler [32]. Compared to $\text{Ni}(\text{CO})_4$ which exhibits efficient photodissociation, the heteroleptic $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ complex was found to be relatively stable. Following excitation at 356 nm, the complex showed red emission with a band maximum at 650 nm (dotted line in Figure 2) both at room temperature in fluid acetonitrile and at 77 K. At such low temperature, the luminescence quantum yield was 10^{-3} . The excitation spectrum roughly matched the absorption spectrum (solid line in Figure 2). Similar to the complexes discussed above, there is a large shift between the emission band maximum and the maximum of the energetically lowest detectable absorption band. It was noted that in principle the lowest energy transitions could be either MLCT or intraligand (IL) transitions on the arylphosphine ligands (as observed previously in some Cu(I) arylphosphine complexes), but the assignment to $^3\text{MLCT}$ states was favored. From the very large shift between absorption and emission (Figure 2) it was inferred that excitation to the emissive state is associated with a considerable structural change, in analogy to what is commonly observed for Cu(I) polypyridyl complexes upon MLCT excitation.



Scheme 2. Molecular structure of a Ni(0) complex with *N*-heterocyclic carbene ligands [33].

In 2003 the same investigators reported on an interesting conceptual advance from phosphine to *N*-heterocyclic carbene (NHC) ligands (Scheme 2), leading them from the previously investigated $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ to the new $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ complex (dbiy = 1,3-di-*t*-butylimidazol-2-ylidene) [33]. NHC ligands are comparatively weak π -acceptor ligands and hence MLCT transitions are expected to occur at higher energies than with phosphines. Indeed, the emission band maximum for $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ in CH_3CN was at 510 nm at room temperature (Figure 3) [33], compared to 650 nm for $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ under identical conditions (Figure 2) [32]. Due to lack of significant overlap between the lowest-energetic MLCT absorption and the MLCT luminescence band, the emissive state was assigned to a triplet, and it was noted that this is somewhat intriguing because Ni(0) should not exert a strong heavy atom effect. On the other hand, it was also noted that this behavior is in line with isoelectronic Cu(I) complexes.

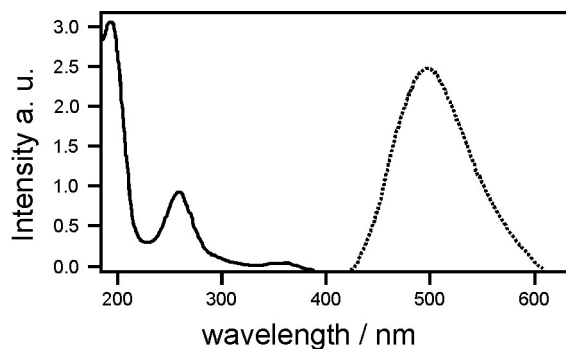
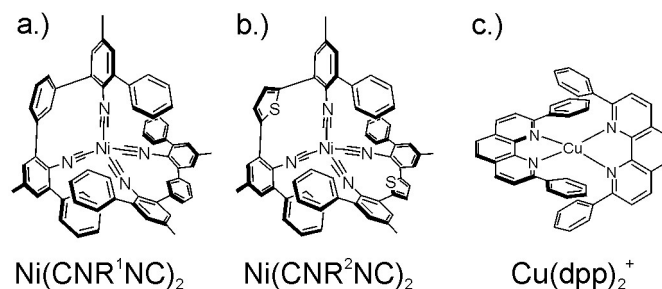


Figure 3. Absorption (solid line) and luminescence (dotted line) spectra of $\text{Ni(CO)}_2(\text{dbiy})_2$ in CH_3CN under Ar at room temperature [33].



Scheme 3. Molecular structures of two Ni(0) complexes with bidentate isocyanide ligands (a, CNR^1NC ; b, CNR^2NC) and (c) the Cu(dpp)_2^+ parent complex (dpp = 2,9-diphenyl-1,10-phenanthroline) [28].

The next publication on luminescent Ni(0) complexes appeared in 2017 after a break of 14 years, when we reported on two homoleptic complexes with bidentate isocyanide ligands (Scheme 3a/b) [28]. We had previously discovered that such chelating isocyanides provide access to relatively robust d^6 metal complexes made from Cr(0) and Mo(0) that are luminescent analogues of well-known Ru(II) polypyridyl and cyclometalated Ir(III) complexes [34–38]. The molecular design of the Ni(0) complexes in Scheme 3a/b was inspired by the structure of the Cu(dpp)_2^+ parent complex (dpp = 2,9-diphenyl-1,10-phenanthroline), in which the phenyl-substituents in α -position to the ligating N-atoms are used to impede planarization in the MLCT state, thereby enhancing the luminescence properties [1, 5]. $^3\text{MLCT}$ luminescence is indeed observed, albeit only in frozen solvent matrices at 77 K, but not at room temperature (dotted lines in Figure 4) [28]. The cyclic voltammogram recorded in THF for one of the two complexes resembles some of the voltammograms typically reported for Cu(I) bis(diimine) complexes. These undergo a (reversible) change in coordination number upon oxidation to Cu(II) , as exploited in molecular machines [39]. This observation and the lack of MLCT luminescence at room temperature suggest that the ligand design is sub-optimal, in that planarization in the MLCT state is not sufficiently suppressed. Alternatively, it is conceivable that hemi-lability of the diisocyanide ligands represents an important pathway for nonradiative excited-state relaxation.

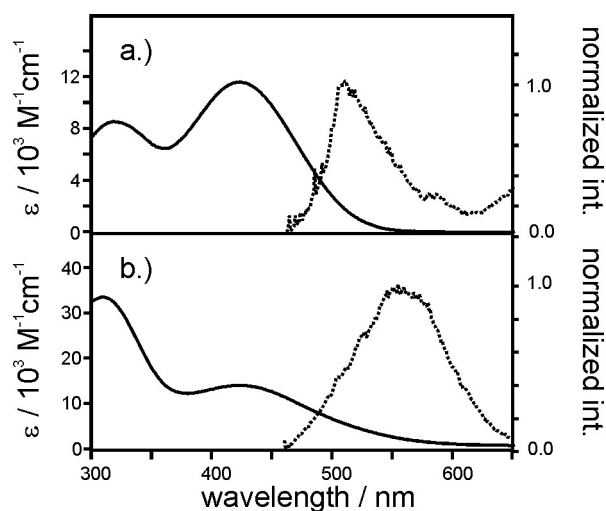


Figure 4. Absorption (solid lines) and luminescence (dotted lines) spectra of the two Ni(0) complexes from Scheme 3 (a, Ni(CNR¹NC)₂; b, Ni(CNR²NC)₂). Absorption was recorded in THF at room temperature, emission in toluene at 77 K [28].

3. Summary and conclusions

While luminescent Cu(I) complexes have received enormous attention resulting in hundreds of publications, there seem to be only 6 papers reporting luminescence of isoelectronic Ni(0) complexes. The first study appeared in 1970 [29], and then there were scattered reports by different researchers in 1985 [30], 1997 [31]; 2000 [32], 2003 [33], and 2017 [28]. Ligand classes that have been used so far comprise phosphines [29-32], phosphites [30, 31], arsines [31], antimonines [31], *N*-heterocyclic carbenes [33], and isocyanides [28]. In most cases, monodentate ligands were employed [29-33], but some bidentate chelators were also used [28, 31]. Emission in the solid state (at 77 K or at 298 K) was observable in all cases, but luminescence in fluid solution at room temperature is rare. The luminescence originates from an MLCT excited state in most cases [28, 31-33], but it was noted that several of the used ligands could have π - π^* transitions that are energetically close [32]. In one early study, the luminescence was attributed to coordinatively un-saturated NiL₃ species exhibiting an emissive $d \rightarrow p$ transition [30]. The long luminescence lifetimes detected in most cases are compatible with spin-forbidden transitions from triplet excited states. Table 1 summarizes luminescence data for all Ni(0) complexes for which a minimum level of detail is known; this excludes some of the very early compounds [29]. Assignment of the luminescence transitions proved somewhat challenging in many of the Ni(0) cases studied so far. For several examples it was not clear whether MLCT, intraligand, or some other type of transition is responsible for the emission, and future studies will have to address this issue both from an experimental and computational perspective.

Table 1. Luminescence properties of Ni(0) complexes (λ_{max} = emission band maximum; τ = luminescence lifetime; ϕ = luminescence quantum yield).

compound	λ_{max} / nm	Stokes shift / cm^{-1}	τ / μs	ϕ (%)	assignment
Ni(PPh ₃) ₄	740 ^a				NiL ₃ , d→p
Ni(P(O- <i>o</i> -cresyl) ₃) ₃	645 ^a		5.13 ^a	0.293 ^a	NiL ₃ , d→p
Ni(P(OPh) ₃) ₄	634 ^b		32.4 ^b		MLCT
Ni(AsPh ₃) ₄	620 ^b	~11'000 cm^{-1}	20.2 ^b		MLCT
Ni(SbPh ₃) ₄	634 ^b	~11'000 cm^{-1}	9.7 ^b		MLCT
Ni(dppe) ₂	613 ^b	~11'000 cm^{-1}	7.6 ^b		MLCT
Ni(CO) ₂ (PPh ₃) ₂	650 ^c			0.1 ^c	MLCT
Ni(CO) ₂ (SbPh ₃) ₂	639 ^b				MLCT
Ni(CO) ₂ (dbiy) ₂	510 ^d				MLCT
Ni(CNR ¹ NC) ₂	520 ^e		0.20- 1.10 ^e		MLCT
Ni(CNR ² NC) ₂	560 ^e		0.23- 1.20 ^e		MLCT

^a In N₂-saturated THF at 25 °C, from ref. [30]; ^b in the solid state at room temperature, from ref. [31]; ^c in the solid state at 77 K, from ref. [33]; in CH₃CN under Ar at room temperature, from ref. [33]; ^e in frozen toluene at 77 K, from ref. [28].

The small number of known luminescent Ni(0) complexes compared to isoelectronic Cu(I) species most likely reflects the fact that Ni(0) complexes are substantially more readily oxidizable, making their synthesis and characterization more tricky and perhaps limiting their (immediately evident) application potential relative to Cu(I) complexes. Nevertheless it seems worthwhile to explore the possibility of obtaining Ni(0) complexes with improved luminescence properties. Currently, Ni(0) ³MLCT emission is restricted to the solid state or to cryogenic temperatures in most cases, and large Stokes shifts indicate sizeable excited-state distortions. The strategies applied so successfully in Cu(I) bis(diimine) complexes to suppress excited-state distortions should in principle be applicable to Ni(0) complexes as well [1, 5]. The step from monodentate to chelating bidentate ligands is a first advance in that direction [28, 31], and future avenues could include rigidification of such chelators, introduction of sterically more demanding groups, and the synthesis of heteroleptic complexes made from two different types of chelating ligands.

Some of the many known Cu(I) complexes have remarkably good luminescence properties, and one may of course question whether Ni(0) complexes will ever perform equally well. However, one aspect in which Ni(0) complexes with sufficiently long-lived excited states are likely to be highly competitive with Cu(I) species is their reducing power in the emissive ³MLCT state [28], and this could be of interest for photoredox applications.

Currently, there is yet significant room for improvement regarding the luminescence properties of Ni(0) complexes, but the same is true for many other emitters made from non-precious metals. In addition to the abovementioned Cr(0) [35], Mo(0) [34], and W(0) isocyanide complexes [36, 40, 41], recent promising discoveries include for example Fe(II) [42], Fe(III) [43], Cr(III) [37, 44, 45], Zr(IV) [46], and Ce(IV) complexes [47, 48].

Acknowledgments

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